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Physical Basis of Fragility

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Physical Basis of Fragility

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Abstract

Fragility of glass-forming liquids in the supercooled region is considered in the context of a defect diffusion theory. It is shown that a necessary condition that a liquid be "fragile" is that there is an attractive interaction between the mobile defects i.e. that the defects cluster with falling temperature. The relationship between the model parameters and a widely used fragility index is described. Each of the model parameters provides a contribution to and insight into the fragility value. The behavior of exceptional cases, such as orientationally disordered crystals and aliphatic monohydric alcohols, is also naturally accounted for in terms of the model.

Introduction

Over the years, the concept of fragility has become a useful means of characterizing super-cooled liquids. The term "fragile" appears to have been introduced by Angell in 1985.[1] One way of evaluating fragility has been to construct graphical fragility plots where the logarithm of a dynamical quantity such as electrical relaxation time, viscosity or resistivity has been plotted vs. T_g/T where T_g is the glass transition temperature.[1] Attempts to define fragility quantitatively have been made with varying amounts of success.[2-4] These definitions include both T_o/T_g and D where T_o and D are constants in the empirical Vogel-Fulcher-Tammann equation[5]

$$x = x_o \exp\left(\frac{DT_o}{T - T_o}\right) \qquad (1)$$

and x is a dynamical quantity such as electrical relaxation time, viscosity or resistivity. At present, it appears that the best definition of fragility is given by the slope of a graphical fragility plot at $T = T_g$ i.e. the apparent activation enthalpy at T_g[6]

$$m = \left(\frac{\partial \log x}{\partial (T_g/T)}\right)_{T_g}. \qquad (2)$$

In this Letter, a recently generalized defect diffusion model[7,8] (DDM) is used to interpret and predict the fragility of a liquid using eq. (2). The results appear to represent the first physical model of fragility.

The Defect Diffusion Model

In the defect diffusion model, a dipole reorients or an ion jumps instantaneously when it is encountered by a mobile "defect." The characteristics of the dynamical processes, then, are determined by the flux of mobile defects, $F(t)$, into each site.

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If $N(t)$ is the number of distinct sites a random walking defect visits within a time t and c_m is the concentration of mobile defects, $F(t) = c_m N(t)$. In the limit of a large number of defects, the relaxation law is

$$\phi(t) = \exp[-c_m N(t)]. \qquad (3)$$

In three dimensions, $N(t)$ is proportional to t if the mean time between defect hops, $<t>$, is finite. However, if $<t>$ is infinite, $N(t)$ is proportional to t^β where $\beta \leq 1$ is the stretched exponential parameter. Consequently, the relaxation law can be written

$$\phi(t) = \exp(-c_m \lambda t^\beta) \equiv \exp(-[t/\tau_{DD}]^\beta) \qquad (4)$$

where λ is related to the dynamics of the defects. The mean dipole relaxation time can thus be written as

$$\tau_{DD} = (\lambda c_m)^{-1/\beta} = c_m^{-1/\beta} \tau_o \qquad (5)$$

where $\tau_o = \lambda^{-1/\beta}$.

If the mobile defects cluster (or correlate their motion) into immobile aggregates as the temperature is lowered (or as pressure increases), then the number of mobile defects will decrease as temperature decreases (or pressure increases). For simplicity, the assumption is made that only single defects of concentration c_1 are mobile. Consequently, c_m is identified with c_1 in eq. (5). To have a single defect at a site, one must first have a defect there with probability c (c is the total defect concentration.) and also have none of the z sites within a correlation volume simultaneously occupied, i.e.

$$c_1 = c(1-c)^z \qquad (6)$$

with $z = (\xi/d)^3$, where ξ is the defect-defect pair correlation length, and d is the nearest neighbor lattice spacing. In a mean field lattice gas model, the correlation length, ξ,

grows near and above the critical temperature T_C as $\xi(T) \approx L\left(\dfrac{T_C}{T-T_C}\right)^{1.5\gamma}$ where L^2 is the

second moment of the direct correlation function $C(\mathbf{r})$ between the defects[9] (i.e. the short-range Ornstein Zernike correlation length), T_C is the temperature at which single defects condense to form a defect liquid and γ is a constant that describes local field effects. In the present formulation, it is assumed that a divergence of ξ occurs for any value of the defect concentration, c, and not just the "critical" value $c = 0.5$. Finally, it is assumed that d is given by $d^3 = d_0^3(1-\delta(T,P))$ for isotropic materials where $\delta(T,P)$ is the fractional decrease in the volume of the material as pressure increases or temperature decreases and d_0 is the mean lattice spacing at zero pressure and an arbitrary reference temperature. The time scale in the stretched exponential can now be expressed as,

$$\tau_{DD} \approx c_1^{-1/\beta}\tau_0 = c^{-1/\beta}\tau_0 \exp\left(\frac{BT_C^{1.5\gamma}}{(T-T_C)^{1.5\gamma}(1-\delta(T,P))}\right) \tag{7}$$

and B is given by

$$B = -\frac{L^3 \ln(1-c)}{\beta d_0^3}. \tag{8}$$

If τ_0 (and hence λ) and c may be assumed constant, eq. (7) can be written as

$$\tau_{DD} = A_\tau \exp\left(\frac{BT_C^{1.5\gamma}}{(T-T_C)^{1.5\gamma}(1-\delta)}\right) \tag{9}$$

where A_τ is a constant. Eq. (9) has been applied to dielectric relaxation and ionic conductivity data.[10,11] These equations are valid for processes in the region close to and above T_g. For many materials, it appears that a change in dynamics occurs at about 1.2

$T_g{}^{12}$ and thus the present formulation would not be expected to apply above 1.2 T_g in those cases.

When the mobile defects do not attract each other and hence do not cluster, then eqs. (7) or (9) are no longer appropriate. In this case, the concentration of mobile defects, c_m, is constant and the relaxation is dominated by the dynamics of the defects. The model assumes that the defects jump over a distribution of barriers having a minimum height Δ_0. The fastest jump frequency of the defects, f, is given by the usual expression

$$f = f_0 \exp\left(-\frac{\Delta_0}{kT}\right). \tag{10}$$

Bendler and Shlesinger have shown that this gives rise to the following relaxation law[13]

$$\phi(t) = \exp\left[\frac{-c_m \sin(\pi\beta)(ft)^\beta}{G(0,1)\pi\beta\Gamma(1+\beta)}\right] \tag{11}$$

where $G(0,1)$ is a constant depending on the lattice structure. Comparison of eqs. (4), (5) and (11) leads to the following expression for τ_{DD}

$$\tau_{DD} = \left(\frac{c_m \sin(\pi\beta)}{G(0,1)\pi\beta\Gamma(1+\beta)}\right)^{-1/\beta} f^{-1} \tag{12}$$

which can be rewritten as

$$\tau_{DD} = \tau_{pre} \exp\left(\frac{\Delta_0}{kT}\right). \tag{13}$$

Consequently, when the defects do not cluster, the DDM leads to an Arrhenius expression for τ_{DD}.

The Defect Diffusion Model and Fragility

We now consider fragile liquids where eq. (9) applies. Ignoring small temperature effects in $(1-\delta)$, substitution of eq. (9) into eq. (2) with $x = \tau_{DD}$ yields the following equation for the fragility of a supercooled liquid near T_g

$$m_{DD} = \frac{0.65 T_C^{1.5\gamma} B\gamma}{T_g^{1.5\gamma}\left(1 - \dfrac{T_C}{T_g}\right)^{1+1.5\gamma}} \tag{14}$$

Another useful form can be obtained by substituting eq. (8) into eq. (14)

$$m_{DD} = -\frac{0.65 T_C^{1.5\gamma} L^3 \ln(1-c)\gamma}{\beta d_0^3 T_g^{1.5\gamma}\left(1 - \dfrac{T_C}{T_g}\right)^{1+1.5\gamma}}. \tag{15}$$

(When x corresponds to viscosity or resistivity, the equation for fragility will be slightly modified because of temperature dependencies appearing in the pre-exponential factor for those quantities.)

From eqs. (14) and (15), fragility is seen to be directly related to the critical temperature, T_C. The central assumption of the DDM is that the fluid contains mobile single defects. When these mobile single defects attract each other, they form immobile clusters as temperature falls or pressure increases and eventually complete aggregation is achieved at T_C. T_C is a thermodynamic defect transition and is the temperature at which the number of single defects falls to zero. A real fluid never reaches T_C because the glass transition intervenes.[7] In the Bragg-Williams approximation (with equal occupation of A and B sites) for a nearest neighbor lattice gas, the critical temperature is[8,14]

$$T_C = \frac{\upsilon \, \Delta\varepsilon}{4 k_B} \tag{16}$$

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where v is the number of near neighbors, $\Delta\varepsilon$ is the attractive interaction energy between the defects and k_B is Boltzmann's constant. Consequently, if all other terms in eqs. (14) and (15) are constant, the more strongly the defects attract one another, the higher is T_C and the more fragile is the liquid.

Finally, as shown above, when the defects do not attract, but repel, the DDM leads to Arrhenius behavior and this is characteristic of a "strong" liquid.[1] Thus, in the framework of generalized Vogel theory, a liquid is "fragile" if there is an attractive interaction between the defects i.e. the defects begin to cluster as temperature is lowered.

Of course, it is also clear from eqs. (14) and (15) that other quantities influence the fragility. For example, the value of T_g affects m. This is important because it shows that the fragility depends upon the definition of T_g, e.g. calorimetric values vs. the temperature at which the relaxation time has a specified value, etc.

Next, it is significant that the values of T_g have an effect on m opposite to that of T_C e.g. $T_C^{1.5\gamma}$ appears in the numerator while $T_g^{1.5\gamma}$ appears in the denominator, etc. This result lends support to the usage of the coefficient D in eq. (1) and T_o/T_g as indicators of the fragility.[3] Specifically, when $\gamma = 2/3$, the Vogel-Fulcher equation is obtained. In that case, $D = B$, and it is apparent from eq. (14) that the fragility is proportional to B. In addition, when $\gamma = 2/3$, $T_C = T_o$ and it is clear from eq. (14) that m increases as the ratio T_o/T_g increases.

Perhaps most importantly, in generalized Vogel theory B, and hence D, has a physical basis via eq. (8). The effect of the lengths is reasonable since a larger L and a smaller d_0 are expected to lead to a greater fragility. A larger L implies that the defects interact over a longer distance (i.e., they are more cooperative in their motion) thereby

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increasing the fragility. A smaller d_0 leads to the same effect. Also, the higher the total concentration of defects, the greater is the fragility. This is also reasonable since a higher total concentration of defects will increase the probability of clustering and raise the fragility. Finally, eq. (15) illustrates that the smaller the stretched exponential parameter, the greater is the fragility.

The Model Applied to Real Systems

Attempts to understand fragility in the context of real systems have been made by many authors.[1-4,6,15-18] For example, Bohmer et al. have evaluated various types of data for about 70 glass formers.[6] They established the following empirical relationship between β and m

$$m_{empirical} = 250 - 320\beta \qquad (17)$$

Thus, the smaller the stretched exponential parameter, β, the greater is the fragility, m. As discussed above, this is the general trend predicted by the DDM. However, as is evident from eq. (15), the DDM predicts a different mathematical dependence of m on β. The decrease of m as β increases is hyperbolic rather than linear. However, hyperbolic behavior is predicted only if the quantities other than m and β in eq. (15) are constant i.e. material independent. This would not be expected in general since the defect concentration, correlation length, etc. should be material dependent. Consequently, the DDM does not predict universality. This is in accord with the results of the analysis by Bohmer et al. who noted a large number of "exceptions" to the empirical result of eq. (17).[6]

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For example, certain alcohols are well outside the range of applicability of eq. (17). In the DDM picture, there is no causal connection between m and β. Non-Debye behavior is due to spatial heterogeneity in the barrier hopping distribution encountered by the defects.[8] The aliphatic monohydric alcohols are Debye-like in their relaxation behavior (i.e., β is large, approaching 1.0), but are found to be rather fragile in their specific heat jumps and less so in their relaxation properties. This is easy to interpret in the DDM. The barrier distribution is narrow in these hydrogen bonded alcohols, so that the defects do not find themselves in long-lived trapping sites. On the other hand, the defects attract each other weakly, exhibit a weak tendency to cluster, and thus display moderate values of the fragility.

To illustrate that eq. (15) is capable of reproducing the data quantitatively, it was assumed that all of the quantities except β on the right hand side are constants, independent of the material and that the constants together lead to a value of 42. Again, this does not capture the spirit of the DMM since each material should have a different set of constants. Nonetheless, the curve represented by $m_{DD} = 42/\beta$ and all of the data for polymers and alcohols from Ref. 6 are plotted in Fig. 1. It is clear that the general trend of the data is reproduced by this application of the defect diffusion model.

To show that order of magnitude is reasonable, the following estimates were considered. First, it was assumed that $T_C/T_g \approx 0.75$. This is supported by results for six different materials.[7] Next, the usual assumption was made that $\gamma = 1$. With these assumptions, it follows that $m_{DD} \approx 13.5B$. Consequently, it follows that

$$-\frac{L^3 \ln(1-c)}{d_0^{\,3}} \approx 3.1 \qquad (18)$$

A reasonable set of parameters that satisfies this condition (and thus reproduces the data) is $c \approx 0.1$ and $L/d_0 \approx 3.1$.

It is clear from the data in Ref. 6 and the trend shown by the curve in Fig. 1 of the present Letter that for orientationally disordered glasses (ODICs), "complex" molecules, "simple" molecules, molten salts and networks, a single curve cannot reproduce the results. This is consistent with the DMM theory since it is expected that parameters such as the defect concentration, Debye length, nearest neighbor distance, and the ratio T_C/T_g will be different for different materials. For example, it was pointed out in Ref. 6 that ODICs exhibit very non-Debye behavior (i.e., small β) but little fragility. Again, in the DMM theory non-Debye behavior is caused by spatial heterogeneity in the barrier hopping distribution encountered by the defects.[8] ODICs may have significant barrier heterogeneity (i.e., small β), but little or no attraction between defects and thus they will belong to the class of "strong" liquids.

It is interesting to speculate on the nature of the defect-defect interactions. Noteworthy early theoretical treatments of the interaction between lattice defects have been given by Montroll and Potts.[19,20] In the earlier paper, they showed that "like" defects attract and "unlike" defects repel. Experimental studies of dipolar defects in rare earth doped calcium fluoride have proved the existence of clusters of defects.[21] On the other hand, no evidence of clusters is found in alkali metal doped alkaline earth fluorides.[22] (In the alkaline earth fluorides, the simple defects are also immobile.) These are a few examples of an extensive literature that exists concerning defects in solids and their interactions.

An example of a specific polymer defect has been given previously. Detailed studies of the polycarbonate molecule suggest that a mobile carbonate unit (CO_3) is one defect whose motion contributes to the mechanical, dielectric and nuclear magnetic relaxation in the glassy state.[23-25] Other types of defects have not been identified to date. However, it is interesting to speculate on the nature of the defects in other materials. Defects may either be neutral or charged. In the case of neutral defects, the interaction may be Van der Waals in nature, for example. In that case, the defect-defect interaction would be attractive and thus clustering would be expected. The case of charged defects is particularly intriguing. For example, it may be that defects in materials such as SiO_2 or GeO_2 repel one another because they are charged. This would eliminate clustering thereby making the materials "strong" glass-formers.

Summary

The definition of fragility is considered in the context of defect diffusion theory. It is shown that a necessary condition that a liquid be "fragile" is that there is an attractive interaction between the defects i.e. that the defects cluster. The relationship between the model parameters and a widely used fragility index is also described. Each of the model parameters contributes to the fragility in a reasonable manner. The behavior of exceptional cases, such as orientationally disordered crystals and aliphatic monohydric alcohols, is also naturally accounted for in terms of the model.

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Acknowledgments

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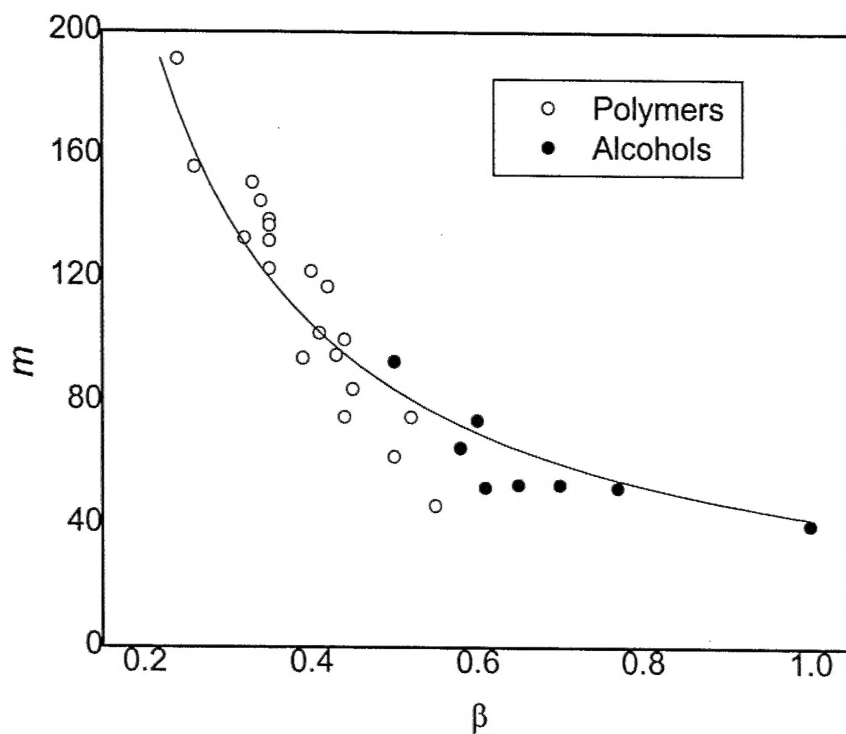
Figure 1. Fragility, m, vs. the stretched exponential parameter, β, for the data for polymers and alcohols from ref. 6. Also shown is the representative curve, $m = 42/\beta$ which is consistent with the DDM.